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(Extractive translation)

Patent Laid-Open Gazette

Patent Laid-Open No. Sho 52-4519

Patent Laid-Open Date: January 13, 1977

Patent Application No. Sho 50-80008

Patent Application Date: June 30, 1975

Inventor: Masahiro Kondo

Applicant: Fuji Fiber Glass Inc.

Title of the Invention: Alkali-proof glass composition

The claims:

1. An alkali-proof glass composition comprising 42-67 % by weight of SiO_2, 4-24 % by weight of Al_2O_3 and 24-34 % by weight of RO wherein R represent at least one or two or more kinds of alkaline earth metal.

Page (2), left column, lines 1-7

The glass composition of the present invention is characterized in that alkali metal oxide which reduce chemical resistance is not included and alkaline earth metal which is fairly effective on alkali resistance is included in a large amount. Also, the glass composition has characteristic that it is inexpensive since it includes no zirconia which is effective on alkali resistance.

of	CaO	24	24	29	26	29	29	20	29	-	-	E -
Glass												
Glass	Al_2O_3	19	24	14	14	19	24	19	9	14	14	
(% by Mass)	MgO	-	-	-	8	-	-	14	-	29	-	
	BaO	-	-	-	-	-	-	-	-	-	29	
Alkali Resistance												
(% of Reduction of Mass)		1.01		0.79		0.67		0.62		0.65	0.67	0.55
0.62	0.54	1.80		3.21								

All of the glass test substances numbered 1 to 10 had a better alkali resistance than E glass.

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metal oxide, a low cost glass composite with excellent resistance to alkalis can be produced. If alkaline earth metal oxides other than CaO are used, such as MgO or BaO, the cost increases somewhat. However, especially in the case of BaO, the alkali resistance is diminished somewhat, but it is still better than E glass. If the amount of alkaline earth metal oxides is less than 24% by mass, it becomes difficult to melt, and the alkali resistance is diminished. However, if the amount of alkali earth metal oxides is greater than 34% by mass, it becomes easy for the glass to lose its transparency. If the amount of Al_2O_3 is less than 4% by mass, it becomes difficult to melt. However, if the amount of Al_2O_3 is greater than 24% by mass, it again becomes difficult to melt, so the amount of Al_2O_3 should be kept in the range 4 to 24%.

Below is a description of the experiments conducted in relation to this invention.

The glass sample used in these experiments was produced by melting a pre-prepared glass base material in a platinum crucible at 1450° C over an electric burner and then cooling it in room temperature air. For the alkali resistance tests, a glass powder pulverized to between 35 and 60 mesh was submerged for 24 hours in an 80° C solution of 1N caustic soda, and then its loss of mass is measured.

		Experiment									
Glass Test Substance Number		1	2	3	4	5	6	7	8	9	10
Comparison											
Experiment											
Composition SiO_2		57	52	57	52	52	47	47	62	57	57

Ingredient	Percent by Mass
SiO_2	42 - 67
RO	24 - 34
Al_2O_3	4 - 24

(The R in the above ingredients must represent at least one or two alkali earth metals.)

The following ratios are the most desirable:

Ingredient	Percent by Mass
SiO_2	52 - 62
RO	24 - 29
Al_2O_3	9 - 24

(The R in the above ingredients must represent at least one or two alkali earth metals.)

The glass composite in this invention does not contain alkali metal oxides which reduce chemical durability, rather it contains large amounts of alkali earth metal oxides which are comparatively more effective at resisting alkalis. Furthermore, because the alkali-resistant glass composite does not contain zirconia, which is well-known for excellent resistance to alkalis, it has a low cost.

If the SiO_2 content of the glass composite in this invention is less than 42% by mass, it becomes difficult to make it into glass. However, if the SiO_2 content is more than 67% by mass, it becomes very difficult to melt, and the alkali-resistance is also diminished.

By using CaO or CaO with one section substituted by Mg as the alkali earth

Detailed Description

1. Name of Invention:

Alkali Resistant Glass Composite

2. Range of Claims for Patent

An alkali-resistant glass composite that is composed of between 42 and 67% (all percentages are by mass) SiO_2, between 4 and 24% Al_2O_3, and between 24 and 34% RO (with the condition that the R must represent at least one or two types of alkali earth metals).

3. Detailed Explanation of Invention

This invention is related to a glass composite that is alkali resistant and that can be made into fibers.

Up until very recently, it has not been very desirable to use E glass fibers as a long lasting (more than 5 years) strengthening agent for cements, mortars, etc., which are known to have a highly bondable matrix containing a large amount of alkali. The E glass fibers are overcome by the alkali content in the bondable matrix, and their strengthening qualities are diminished. The long-term strength of such bondable matrices that have been strengthened with E glass fibers is thus diminished.

The inventors of this invention, as a result of conducting numerous experiments on glass fibers for use as strengthening agents for bondable matrices with high alkali content, have discovered an alkali-resistant glass composite that can be made into fiber, which functions excellently as a long-term strengthening agent. The glass composite falls into the following range of ratios:

Patent Application (1)

June 30, 1975

To the Head of the Patent Bureau:

1. Name of Invention:
   Alkali Resistant Glass Composite

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4. List of Attached Documents
   (1) Detailed Description 1
   (2) Copy of Application 1
   (3) Request for Patent Inquiry 1

(19) Japan Bureau of Patents
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特 許 願

特許庁長官殿

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耐アルカリ性ガラス組成物

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4. 添付書類の目録
(1) 明細書 1通
(2) 特許願副本 1通
(3) 出願審査請求書 1通

50 080008

明 細 書

1. 発明の名称
耐アルカリ性ガラス組成物

2. 特許請求の範囲
重量%で SiO_2 42～67%, Al_2O_3 4～24%, RO 24～34%（但し，Rはアルカリ土類金属の少なくとも一種又は二種以上を表わす。）より成る事を特徴とする耐アルカリ性ガラス組成物。

3. 発明の詳細な説明
本発明は，耐アルカリ性を有する繊維化可能なガラス組成物に関するものである。

極く最近まで，アルカリ含有率の高い接合性マトリックスとして知られているセメント，モルタル等の長期間（5年以上）の補強材として，Eガラス繊維を用いる事は望ましくなかった。Eガラス繊維は，接合性マトリックス中のアルカリ成分に侵され強度劣化をおこし，Eガラスで補強した接合性マトリックスの長期強度が低下するためである。

本発明者等は，アルカリ含有率の高い接合性マトリックスの補強材用ガラス繊維に関する幾多の研究を行なった結果，長期間の補強材として優れている耐アルカリ性を有し，且つ繊維化可能なガラス組成物の一つは次の比率の範囲内に含まれる事を発見した。

含有成分	重量%
SiO_2	42～67
RO	24～34
Al_2O_3	4～24

（但し，上記成分中Rはアルカリ土類金属の少なくとも一種又は二種以上を表わす。）

望ましくは次の比率の範囲内に含まれる。

含有成分	重量%
SiO_2	52～62
RO	24～29
Al_2O_3	9～24

（但し，上記成分中Rはアルカリ土類金属の少なくとも一種又は二種以上を表わす。）

本発明のガラス組成物は，化学的耐久性を低下せしめるアルカリ金属酸化物を含まず，耐アルカリ性に対して比較的効果の大きいアルカリ土類金属酸化物を多量に含む事を特徴とする。又，耐アルカリ性に効果が大きいとして知られているジルコニアを含まない安価な耐アルカリ性ガラス組成物である事を特徴とする。

本発明のガラス組成物において，SiO_2の量を42重量%より少なくするとガラス化が困難となり，同成分量を67重量%より多くすると極めて溶解しにくくなり耐アルカリ性も悪くなる。

アルカリ土類金属酸化物としては，CaOを用いた場合あるいはCaOの一部をMgOに置換した場合が，最もコスト的にも安価な耐アルカリ性の優れたガラス組成物が得られる。CaOを用いないで，他のアルカリ土類金属酸化物例えばMgO，BaOなどを用いた場合，コスト的にも少々高価になり，特にBaOを用いた場合若干耐アルカリ性効果が劣るが，Eガラスよりは優れている。アルカリ土類金属酸化物の量を24重量%より少なくすると溶解しにくくなり耐アルカリ性も悪くなる。又，同成分量を34重量%より多くすると失透を起こしやすくなる。

Al_2O_3の量を4重量%より少なくすると溶解しにくくなる，又，同成分量を24重量%より多くしても溶解しにくくなるのでAl_2O_3の量は4～24重量%の範囲が好ましい。

以下実施例により本発明を説明する。

本実施例に示したガラス試料は，白金ルツボに，前もって調合されたガラス原料を入れ，これを1450°Cの電気炉で3時間溶解した後，室温空冷したものである。耐アルカリ性試験は，80°Cの1N苛性ソーダ溶液に35～60メッシュに粉砕したガラスパウダーを24時間浸漬した後の重量減少率(%)で示した。

ガラス試料番号		実施例 1	2	3	4	5	6	7	8	9	10	比較例
ガラス成分(重量%)	SiO_2	57	52	57	52	52	47	47	62	57	57	Eガラス
	CaO	24	24	29	26	29	29	20	29	—	—	
	Al_2O_3	19	24	14	14	19	24	19	9	14	14	
	MgO	—	—	—	8	—	—	14	—	29	—	
	BaO	—	—	—	—	—	—	—	—	—	29	
耐アルカリ性(重量減少率%)		1.01	0.79	0.67	0.62	0.65	0.67	0.55	0.62	0.54	1.80	3.21

実施例のガラス試料番号1～10のガラスは，いずれもEガラスに比し，耐アルカリ性が優れている。

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Page (2), upper left column, line 8-13

The glass composition of the present invention has high alkali resistance and good fusibility, and is relatively difficult to devitrify and excellent in water resistance, so that it is readily made into fiber, has good processability, and in addition, has high reinforcing ability over a long time even when it is incorporated into cement material with high alkali.

Page (3), upper left column, line 19 - lower right column, line 8

Alkali resistance test was carried out in such a way that a sample was boiled in an aqueous 1N-NaOH solution for 1 hour, and after standing for 6 hour, washed with water and dried, and reduction in weight was measured as compared with the weight of an untreated sample.

The fusibility was evaluated from the total of a fusing temperature (a temperature at a certain viscosity), a time required for completely fusing a sample, easiness of making a sample into fiber, etc. The evaluation result is indicated as follows.

A: Good.
B: A little caution is needed in working.
C: Working is difficult or formation of fiber is very difficult.
(See Tables 1, 2, 3 in this reference.)